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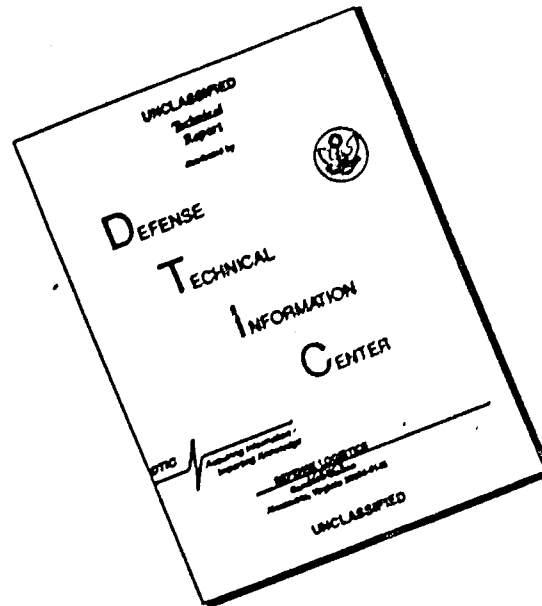
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KINETICS AND MECHANISMS OF THE
THERMAL DECOMPOSITION OF ACETALS

by

M. J. Molera, J. Morcillo, J. Orza, L. Arévalo and E. Gómez-Olea

ANNUAL TECHNICAL REPORT No. 3

Contract No. DA-91-591-EUC-1599-OI-7165-61

1st January 1961 to 31st December 1961

The research reported in this document has been made possible through the support and sponsorship of the U. S. DEPARTMENT OF THE ARMY through its European Research Office.

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ABSTRACT

The experimental part of the work has been carried out in a high vacuum apparatus by the static method. The reactions have been followed by observing the pressure change with time inside the reaction vessel and by quantitative analyses employing a 112 model Perkin Elmer infrared spectrometer. Most samples have been fractionated before analysis, at solid CO_2 and (or) liquid air temperature.

Work done during the period covered by this report may be considered divided into two parts: 1) Sensitization of the thermal decomposition of two acetals, and 2) Detailed study of the nitric oxide inhibited methylal decomposition.

1) Sensitization

The influence of several sensitizers on the thermal decomposition of methylal and dimethyl acetal has been studied.

The activity of ethylene oxide on the normal decomposition of methylal has been tested at several temperatures (421, 478 and 520°C) and starting pressures.

Quantitative analyses of the products formed in the ethylene oxide decomposition have been made under different experimental conditions, as also of the products formed from methylal and ethylene oxide mixtures at different reaction times and at increasing ethylene oxide pressures.

If very small amounts of nitric oxide are added to the methylal-ethylene oxide mixtures, the decomposition rate of the sensitized reaction is greatly reduced, the inhibition being transitory in character.

Both the experiments on the pressure increase rate and the quantitative analyses of the products formed from dimethyl acetal and ethylene oxide mixtures under different experimental conditions at 399°C, prove that the latter compound may be also considered as a sensitizer of the dimethyl acetal decomposition.

Biacetyl has been tested in the 390-520°C range as a possible sensitizer of the methylal decomposition but its influence, if any, is unimportant. However, biacetyl seems to be efficient in sensitizing a reaction in a nitric oxide inhibited methylal decomposition at 520°C.

The question arises whether biacetyl is a true sensitizer of the reaction by starting nitric oxide uninhabitable methylal chains, or whether it is only an apparent sensitization due to consumption in the reaction with biacetyl of the nitric oxide present. In order to elucidate this question detailed experimental work has been done including numerous quantitative analyses.

Di-t-butyl peroxide has been tested in a wide temperature range (168.5 - 527°C) but it seems unsuitable as a sensitizer of methylal decomposition.

2) Study of the nitric oxide inhibited methylal decomposition.

A large number of experiments (about two hundred) have been made in order to elucidate the influence of nitric oxide on the methylal decomposition pressure increase rate at several temperatures, and results prove conclusively that there is no inhibition limit.

These results together with those previously obtained in the 1st and 2nd annual reports on this research, have been thoroughly studied by applying the steady state approximation.

A discussion of the mechanisms resulting from the different reaction possibilities between nitric oxide and one or several of the radicals involved in the normal methylal decomposition proves that the consumption of nitric oxide and other reaction features can not be explained in terms of the inhibition process only. Consequently, a reaction mechanism is proposed in which nitric oxide starts and stops methylal chains.

The proposed mechanism appears to be successful in explaining all the experimental data available, i.e. stoichiometry of the reaction, consumption of nitric oxide during inhibition, products formed, lack of an inhibition limit, etc.

By applying the steady state approximation to the mechanism, we derive an interesting equation which relates the pressure increase rate to the initial amounts of methylal and nitric oxide. This equation depends on several parameters (elementary rate constants or ratios among them) that have been calculated at different temperatures by the trial and error method. They have been used to calculate reasonable values of the corresponding activation energies and frequency factors.

The remarkable agreement between the experimental points and the theoretical curves provides a convincing check of the proposed mechanism.

I. INTRODUCTION

As a contribution to basic research on the kinetics of the thermal decomposition of organic compounds, four acetals were selected for study:

formaldehyde dimethyl acetal (methylal)
formaldehyde diethyl acetal (ethylal)
acetaldehyde dimethyl acetal (dimethyl acetal)
acetaldehyde diethyl acetal (acetal)

During the first year, the normal decompositions of the four acetals were studied. Detailed quantitative analyses were made for different temperatures and reaction times and the kinetic constants determined.

During the second year the methylal chain decomposition was mathematically discussed by applying the steady state approximation to the proposed mechanism. The order of the reaction and several stoichiometric relations among the products were tested experimentally. Moreover some elementary rate constant ratios and the change experienced by several radical concentrations throughout the reaction were evaluated.

During the second year we carried out a detailed experimental study on the inhibited reactions of methylal and dimethyl acetal employing unsaturated compounds and nitric oxide as inhibitors. It was found that considerable differences exist between the olefines and nitric oxide as far as their inhibition behaviour is concerned.

A thorough discussion of the nitric oxide inhibited methylal decomposition has been undertaken during this third year, the aim being to elucidate, if possible, the nature of the so called "complete" inhibition, i.e. whether a molecular rearrangement or whether a residual chain reaction could explain the experimental results obtained. We hoped that a great deal of light would be cast upon the problem by the application of the steady state approximation to several hypothetical mechanisms.

It was also considered advisable to undertake an experimental study of the effect of several sensitizers on the acetal decompositions with the hope of obtaining a deeper understanding of the mechanisms involved by studying the reactions from different points of view.

II. APPARATUS AND METHOD

II.1. Apparatus

The reactions have been studied by the static method in a high vacuum apparatus that has already been described with some detail (1). The silica reaction vessel is kept inside a furnace, the temperature of which is set to $\pm 0.5^{\circ}\text{C}$ by a controller and measured by means of a thermocouple and a slide wire Cambridge potentiometer.

In order to introduce vapour mixtures at accurately measured partial pressures, a change in the experimental device has been made (Fig. 1). Mixtures of the required composition are prepared in the globes by measuring the partial pressures on the manometer. The globes are maintained at a fixed temperature by means of a thermostated bath. The parting factors between the globes and the reaction vessel are previously determined at the chosen reaction temperatures and it is therefore possible to eliminate the errors that might be made in the measurement of the initial pressures, a fact which increases in importance at high initial reaction rates.

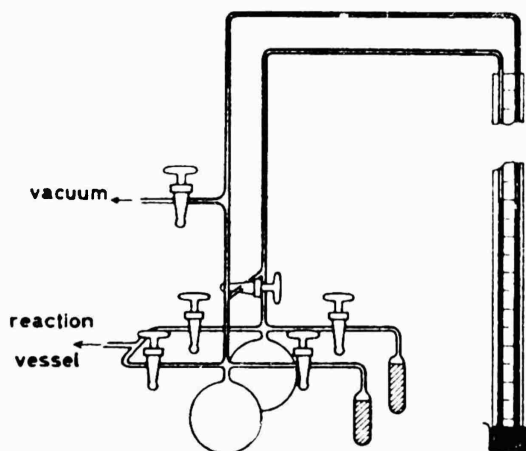


Fig. 1

The decomposition has been followed by measuring the pressure change in the reaction vessel in terms of time and by quantitative analyses with a 112 model Perkin Elmer infrared spectrometer. The samples have been fractionated before analysis, at solid CO_2 or liquid air temperature.

II.2. Preparation and purity of materials

Ethylene oxide

It has been synthesized by the reaction between ethylene chlorhydrin and potassium hydroxide mixed with clean dry sand. The product has been collected at liquid air temperature and purified by fractional distillation.

Other compounds

Nitric oxide has been obtained again as previously described. Biacetyl is a purum grade Fluka chemical. Di-t-butyl peroxide is a purum grade Noury v. der Lande chemical.

II.3. Method of analysis

Qualitative and quantitative analyses have been carried out with a 112 Perkin Elmer infrared spectrometer according to the previously described method (1).

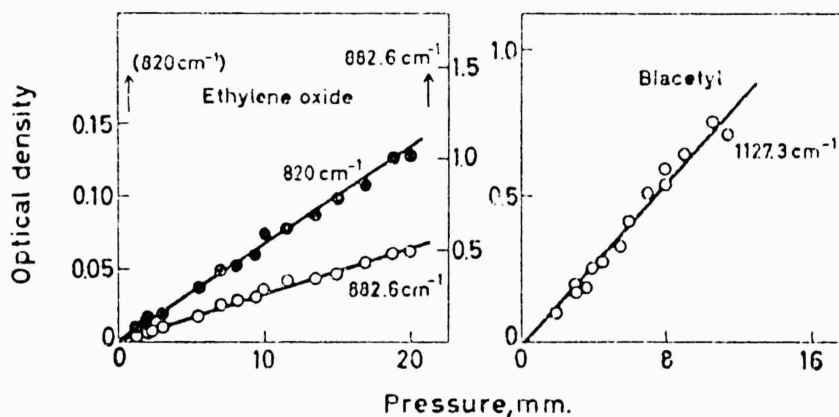


Fig. 2

The ethylene oxide and biacetyl spectra have been determined at several partial pressures, and optical densities have been plotted against partial pressures at convenient wavelengths to obtain the necessary calibration curves (Fig. 2).

III. SENSITIZATION

III.1. Ethylene oxide sensitization of methylal decomposition

III.1.1. Pressure increase-time curves

The sensitizing action of ethylene oxide on the normal decomposition of methylal has been tested at several temperatures (421, 478 and 520°C) and starting pressures. The results obtained for 421°C have been plotted in fig. 3, which shows that methylal decomposes at a higher rate, as the initial pressure of added ethylene oxide increases. For comparative purposes the pressure increase-time curves corresponding to the decompo-

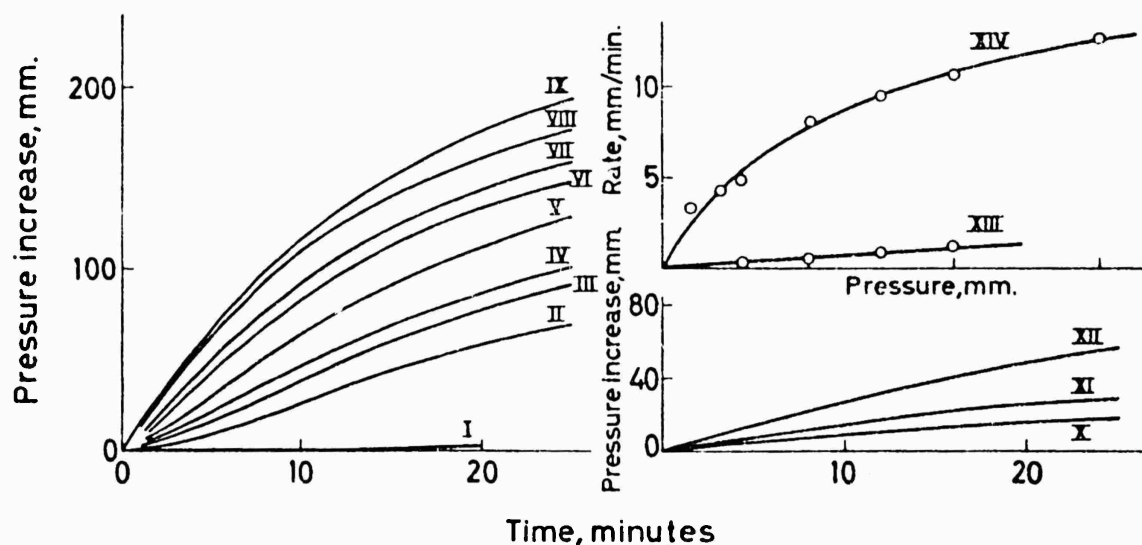


Fig. 3. 421°C. Initial methylal pressure 75 mm and ethylene oxide, curves I - 0; II - 10; III - 21; IV - 28.5; V - 50; VI - 75.5; VII - 99.5; VIII - 150.5; IX - 190 mm. Initial methylal pressure 0 mm, and ethylene oxide curves X - 75.5; XI - 100; XII - 188 mm. - Curve XIII - Ethylene oxide rates. Curve XIV - Methylal and ethylene oxide mixtures rates

sition of thylene oxide alone have been also plotted in the same figure (curves X, XI and XII). The corresponding measured rates are shown in table I.

TABLE I

Temperature, 421°C		
Methylal (mm)	Ethylene oxide (mm)	$\left(\frac{dp}{dt}\right)_0$ (mm/min)
0	75.5	1
0	100	1.3
0	188	2.7
75	0	0
75	10	3.2
75	21	4.3
75	28.5	4.9
75	50	8.2
75	75.5	9.7
75	99.5	10.8
75	150.5	13
75	190	14.5

At the higher sensitizer pressures studied, the rate of reaction increases slowly, in all probability largely due to the decomposition of the large amounts of ethylene oxide that are present, rather than to an increase in the decomposition of methylal itself.

III.1.2. Analyses

In the ethylene oxide sensitized methylal decomposition most of the reaction products appear to be qualitatively the same as those obtained from the normal decomposition. By infrared spectrometry only ketene has been detected as a new product.

In order to check which of the products formed are due to decomposition of ethylene oxide as well as their relative amounts under experimental conditions of this research, we have undertaken several experiments (table II, fig. 4) at 421°C. Analytical samples have been taken by direct parting between the reaction vessel and the infrared analysis cell. Ab-

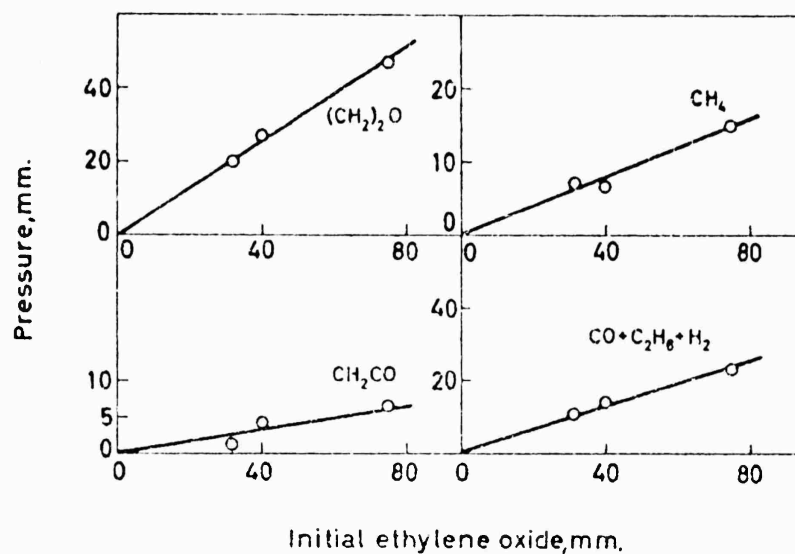


Fig. 4. 421°C. Ethylene oxide decomposition products at 20 minutes reaction time

TABLE II

Normal decomposition of ethylene oxide

Reaction time, 20 minutes, 421°C

(pressures in mm)

Initial ethylene oxide	Ethylene oxide (product)	Methane	Ketene	Acetaldehyde	Dif.	Total pressure (sampling)
31.5	20.8	7	0.8	0.3	12.5	39
40	26.5	6.5	4.3	-	14.5	49.5
75	46.8	14.7	6.7	0.8	22.5	92.5

sorption due to ketene overlaps with that due to carbon monoxide; moreover the former is much greater than the latter when compared on the basis of equal partial pressures of both compounds and. consequently, only

the ketene amounts in the samples may be safely calculated. The error introduced by neglecting the presence of carbon monoxide amounts to only a few units per cent in the optical density measurements. Material balances show that the differences under the "dif" heading are mixtures of roughly 75 % CO, 12.5 % H₂ and 12.5 % C₂H₆ which is in agreement with the results obtained by previous investigators (2).

We have carried out quantitative analyses of the products obtained at 20 minutes reaction time in the sensitized decomposition of 75 mm initial pressure methylal with the addition of variable amounts of ethylene oxide at 421°C (Table III, fig. 5). The analyses have been carried out by infrared spectrometry after fractionation of the samples at liquid air temperature.

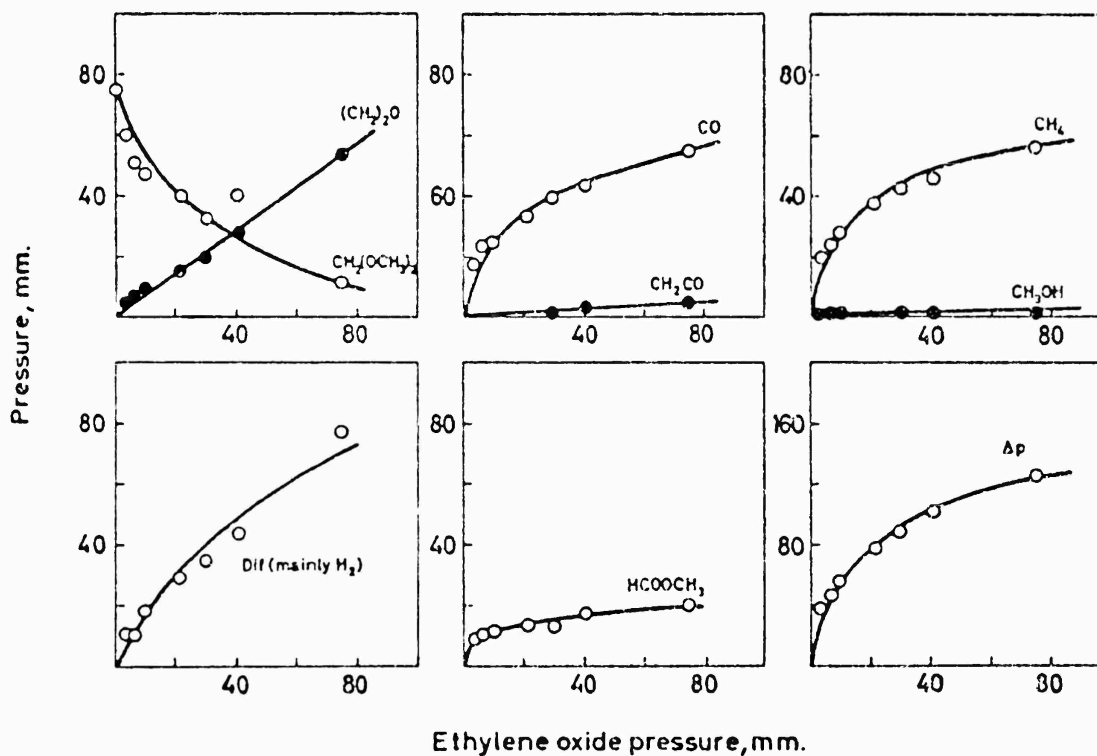


Fig. 5. 421°C. Initial methylal pressure 75 mm. Reaction time 20 minutes.

Some differences have been observed between the total pressure as measured on the manometer and the sum of the products analytically evaluated in the condensed fraction at liquid air temperature. In order to find out the reason for these differences, we have run several blank experiments in which only methylal has been pyrolysed at 421°C. The results obtained, together with those obtained with only ethylene oxide in table II, show that

the observed differences are due to losses of methylal, which is probably absorbed in the tap grease. Material balances between reactants and products confirm this conclusion and, consequently, in that which follows these differences have been systematically added to the amounts of methylal found by infrared spectra.

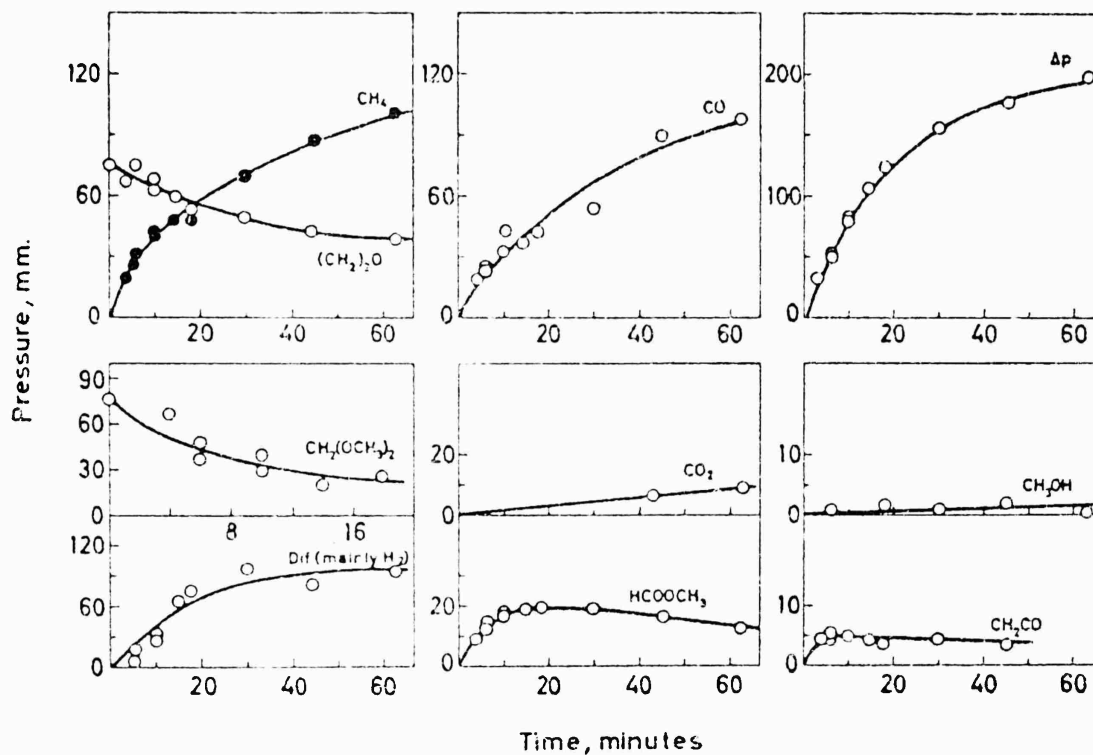


Fig. 6. 421°C. Methylal 75 mm; ethylene oxide 75 mm.

The methylal sensitized decomposition at 421°C has been also studied for different reaction times; the initial partial pressures of methylal and ethylene oxide being 75 mm (table III, fig. 6).

TABLE III

Ethylene oxide sensitized methylal decomposition. Initial methylal pressure 75 mm. temperature 421 °C (pressures in mm)

Initial Ethylene oxide	Time (minutes)	Total pressure (sampling)	Ethylene oxide (product)	Methylal	Methane	Carbon monoxide	Methyl formate	Methyl alcohol	Ketene	Dif (volatile)
3.5	20	117	4.5	60	20	17.5	9	1	-	10.5
6.3	20	127.5	6.5	51	24	23.5	10	1	-	10
9.8	20	139.5	9.5	47	28	24.5	11	1.5	-	18
21.5	20	173.5	15	40	33	33	13.5	-	-	29.5
29.8	20	193	20	32	42.5	39.5	13	1	1.5	34.5
40.5	20	216.5	28.5	40	46	43.5	17.5	1	3.5	43.5
75	4	183	67	67	19	17	9	-	4.3	-
75	6	200	42	36.5	26.5	24	12.5	-	4.5	17
75	6	200	76	48	31.5	25	14	0.8	5.4	5
75	10	233.5	68	29.5	42	41.5	18	-	5	26
75	10	233	63	40	42	32	17.5	-	5	33.5
75	14	257	58.5	20	48	37.5	18.5	-	4.2	65
75	18	273	53	25.5	49	42	19.5	1.8	3.6	77
75	30	305.5	50	-	69.5	54	19	0.8	4.3	99
75	45	325	43	-	85.5	90	16	1.7	3.6	80
75	63	348.5	39	-	99	96.5	12.5	0.3	-	96

III.1.3. The influence of nitric oxide

If very small amounts of nitric oxide are added to the methylal-ethylene oxide mixtures, the decomposition rate is greatly reduced showing that nitric oxide is an inhibitor of the reaction. Moreover, the inhibition seems to be transitory, inhibition time depending on the nitric oxide initial partial pressure (Fig. 7).

The question now arises whether the inhibitory effect of nitric oxide is due to its reaction with radicals formed directly from ethylene oxide or whether the methylal chain is actually inhibited by a reaction between NO and the radicals formed from methylal, after sensitization. Some curves corresponding to the action of nitric oxide on ethylene oxide decomposition have been experimentally determined in this research (Fig. 8). A comparatively high temperature (478°C) has been chosen in order to enhance the reaction between them because it is almost unnoticeable at 421°C. According to these results, it is quite obvious that the great rate reduction ob-

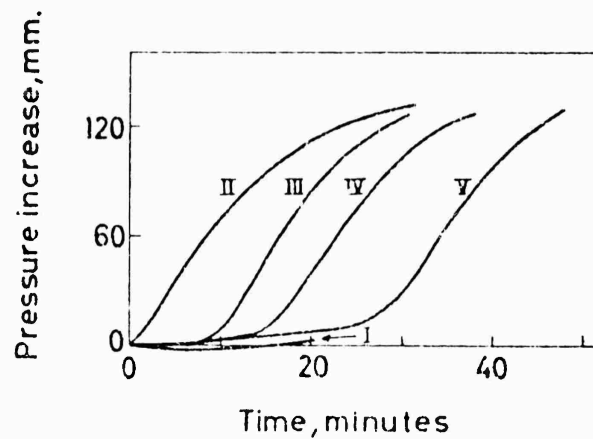


Fig. 7. 421°. Methylal 75 mm.
Ethylene oxide, curves I - 0; II,
III, IV V - 75 mm. Nitric oxide,
curves I - 0; II - 0; III - 1; IV - 2.5;
V - 4 mm

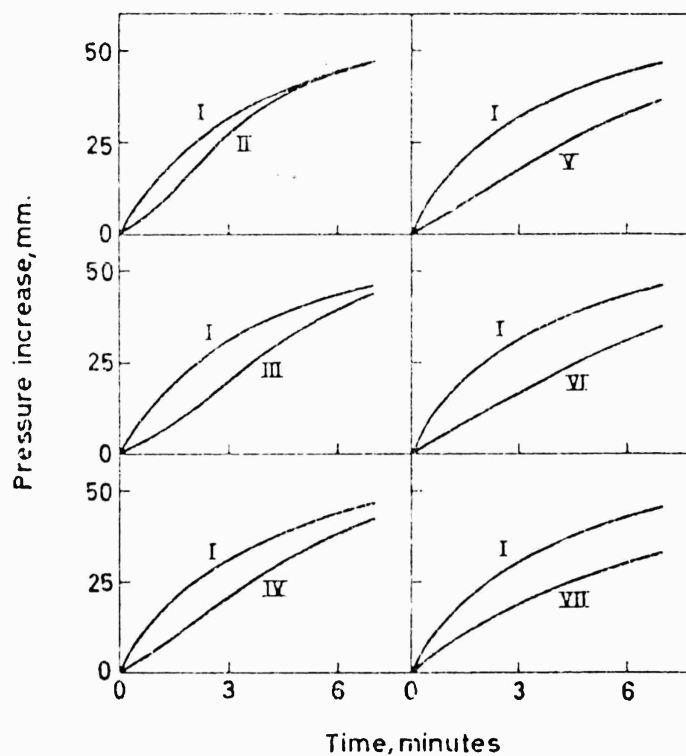


Fig. 8. 478 °C. Ethylene oxide 75 mm.
Nitric oxide, curves I-0; II-2; III-5;
IV-11; V-18, 5; VI-55; VII-200 mm

served in the sensitized methylal decomposition at 421°C in the presence of nitric oxide can not be explained in terms of a reaction between the inhibitor and the ethylene oxide or of any of its decomposition products. The possibility still remains that nitric oxide has reacted with the radicals produced in the ethylene oxide decomposition and that, therefore, no methylal chain was formed.

However, Fletcher and Rollefson (3) and Steacie and Folkins (4) have already studied the inhibitory effect of nitric oxide on ethylene oxide decomposition, following this reaction by pressure increase measurements. According to their results, the induced chain decomposition of the acetaldehyde formed by ethylene oxide isomerization was assumed to be the actual subject of nitric oxide inhibition instead of the main reaction which is responsible for the disappearance of ethylene oxide.

Consequently, a more satisfactory explanation of our experimental results seems to be that here, too, the methylal chain is the actual subject of nitric oxide inhibition after its decomposition has been sensitized by ethylene oxide. The remarkable similarity in the shapes of the Δp -time curves corresponding to the NO inhibited normal decomposition of methylal (5) and of those plotted in fig. 7 greatly supports this assumption.

III.2. Ethylene oxide sensitization of dimethyl acetal decomposition

III.2.1. Pressure increase-time curves

The sensitizing action of ethylene oxide on the thermal decomposition of dimethyl acetal has been studied at 399°C. The curves corresponding

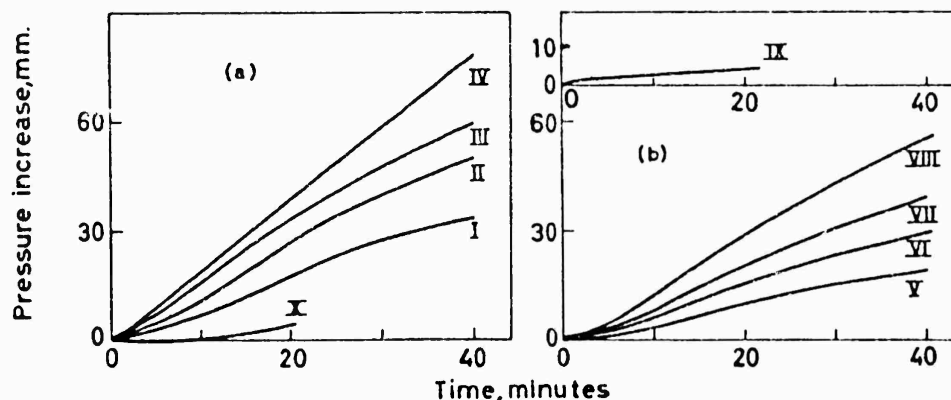


Fig. 9. 399°C. Curves X, I, II, III and IV, dimethyl acetal 75 mm and ethylene oxide 0 - 10 - 20 - 40 - 60 mm respectively. Curves V, VI, VII and VIII ethylene oxide 40 mm and dimethyl acetal 11.5 - 21 - 40 and 61 mm respectively. Curve IX, ethylene oxide 75 mm

to the influence of varying amounts of ethylene oxide on a fixed amount of dimethyl acetal and those obtained with varying amounts of dimethyl acetal and a fixed amount of ethylene oxide are shown in fig. 9 (a) and (b). Curves IX and X belonging to the same figure show that the pressure increase due to the decomposition of either of these two compounds, if decomposed unmixed, is comparatively very small, even at the higher partial pressures considered in these experiments.

III.2.2. Analyses

Quantitative analyses have been effected for different reaction times of the products formed at 399°C in the decomposition of 75 mm initial pressure dimethyl acetal and 40 mm initial pressure ethylene oxide (table IV, fig. 10). Analyses corresponding to the influence of different

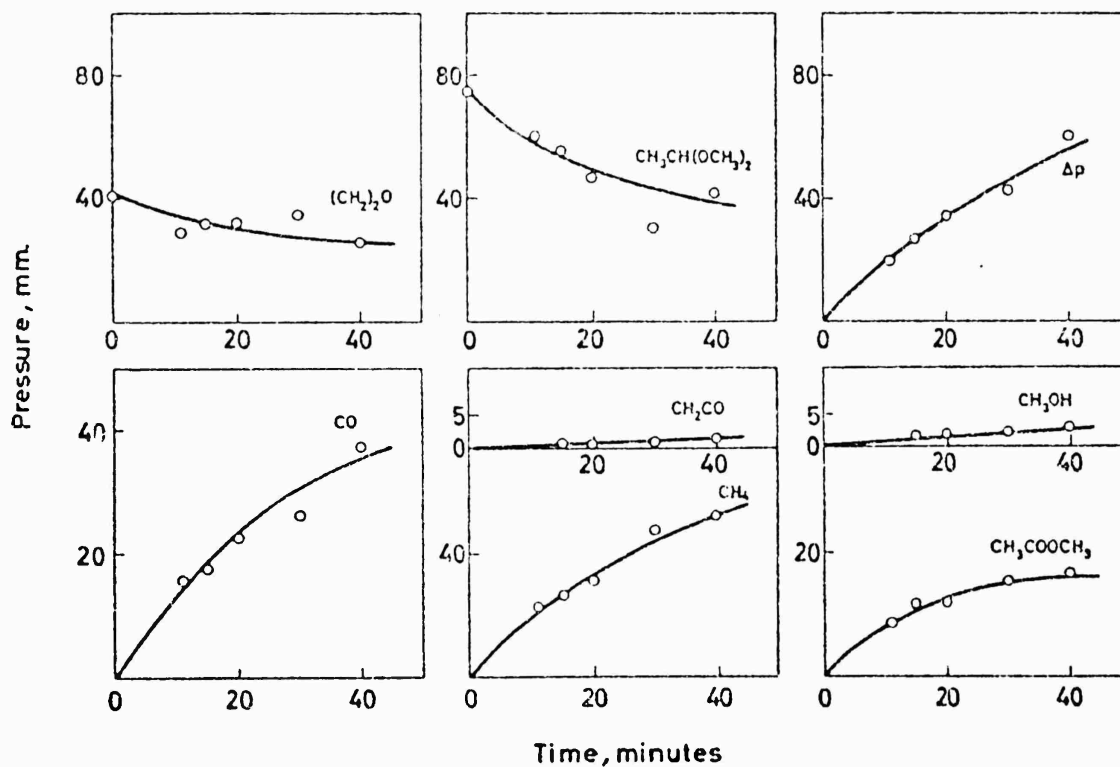


Fig. 10. 399°C. Initial dimethyl acetal pressure 75 mm. Initial ethylene oxide pressure 40 mm

TABLE IV

Ethylene oxide sensitized dimethyl acetal decomposition at 399°C.
Initial dimethyl acetal pressure, 75 mm.
(pressures in mm)

Initial ethylene oxide	Time (minutes)	Ethylene oxide	Dimethyl acetal	Carbon monoxide	Methane	Methyl acetate	Ketene	Methyl alcohol	Vinyl methyl ether	Pressure increase
40	11	29.5	60.5	15.5	22	8.5	-	-	-	20
40	15	32	56	15	26	11.5	0.8	1.5	-	27
40	20	33.5	46.5	22.5	31	12	0.8	1.5	-	34
40	30	35.5	30.5	26	47.5	15.5	0.8	2	-	42
40	40	25.5	42.5	37.5	52	16.5	1.2	2.5	-	60.5
10.3	20	12	49.5	12	22.5	9.5	-	1.2	-	21
20	20	19.5	51.5	14	26	10.5	-	-	-	27.5
31	20	24.5	54.5	13	28.5	10	-	-	1.5	30

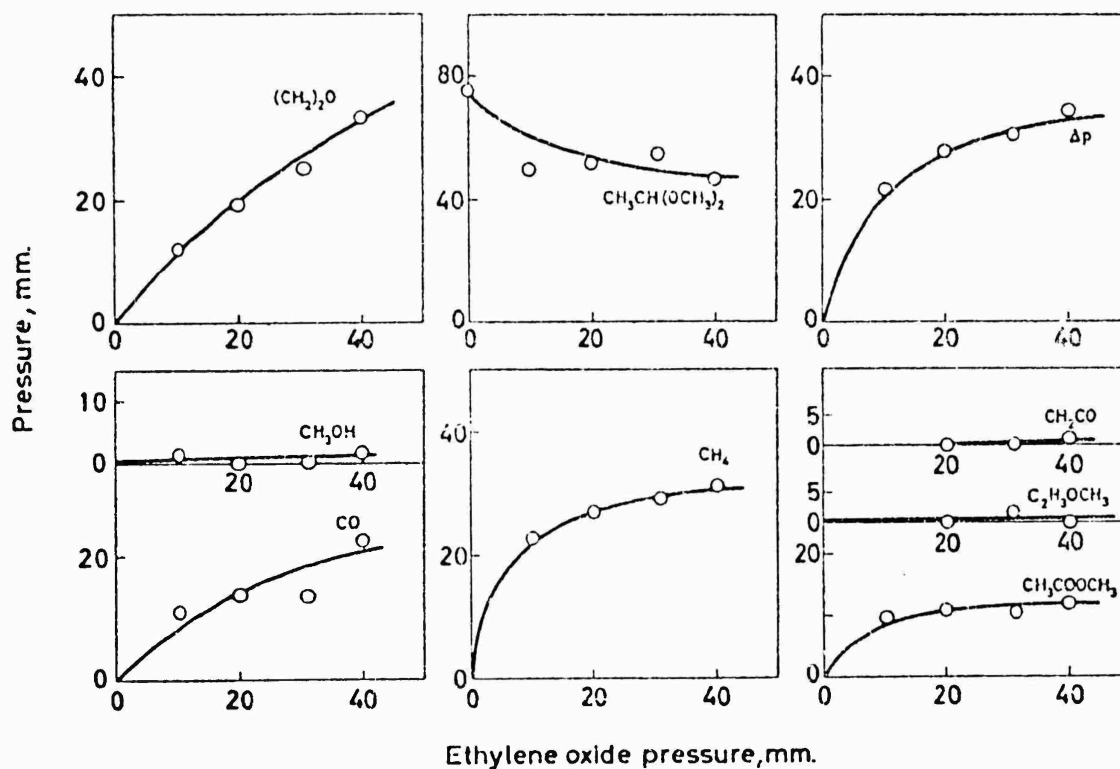


Fig. 11. 399°C. Initial dimethyl acetal pressure 75 mm. Reaction time 20 minutes

amounts of ethylene oxide for a fixed reaction time (20 minutes) on the decomposition of 75 mm initial pressure dimethyl acetal have also been made (table IV, fig. 11).

It seems that the products formed are qualitatively the same as those obtained in the normal dimethyl acetal decomposition. A small amount of ketene formed in the decomposition of ethylene oxide has been found among the products. Other products, such as hydrogen, ethane and acetaldehyde, which are usually formed in the normal decomposition of ethylene oxide, have not been detected owing to the amounts of the latter compound used up during the reaction.

III.3. Biacetyl sensitization of methylal decomposition

III.3.1. Pressure increase-time curves

Experiments have been made at 390, 424, 486 and 520°C in order to test whether biacetyl may be considered as a methylal decomposition sensitizer or otherwise. As an example, the results obtained at 520°C have been plotted in fig. 12 showing that both methylal and biacetyl decompose at rates of the same order of magnitude and that the influence of biacetyl on the decomposition of methylal, if any, is unimportant.

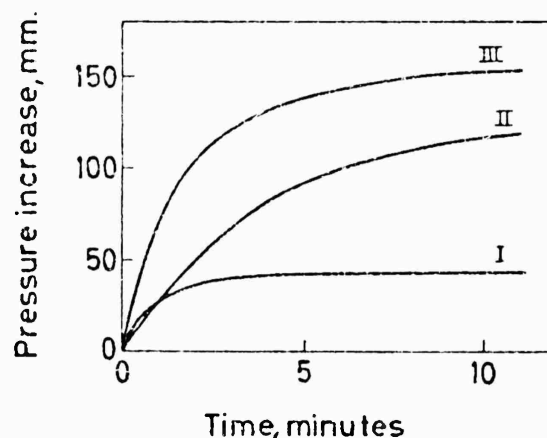


Fig. 12. 520°C. Curve I, biacetyl 30 mm. Curve II, methylal 75 mm. Curve III biacetyl 30 mm plus methylal 75 mm

Klute and Walters (6) have reported that nitric oxide does not inhibit biacetyl decomposition. Consequently, the possibility of studying whether

biacetyl is a sensitizer of the nitric oxide inhibited acetal decomposition has been considered. The results obtained are plotted in figures 13 to 17.

Fig. 13 shows that if a fixed amount of biacetyl (15 mm) is added at 520°C to the decomposing mixture corresponding to the nitric oxide (5 mm) inhibited methylal (75 mm) pyrolysis at different reaction times, the pressure increase-time curves suddenly shift towards greater pressure increases.

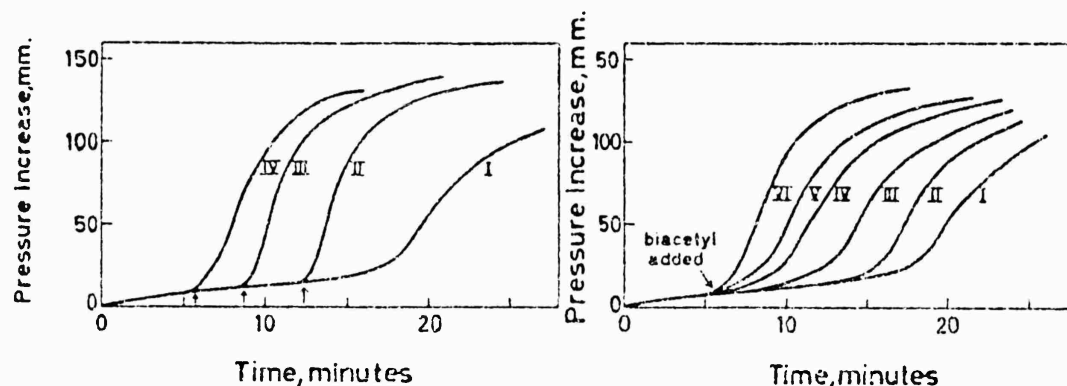


Fig. 13. 520°C. Curve I, initial pressures; methylal 75 mm, nitric oxide 5 mm. Curves II, III and IV: effect of a further addition of biacetyl 15 mm at the times shown by the arrows

Fig. 14. 520°C. Initial pressures, methylal 75 mm, nitric oxide 5 mm. Curves I - 0; II - 5; III - 6.5; IV - 8; V - 10; VI - 15 mm biacetyl added at 5' 30"

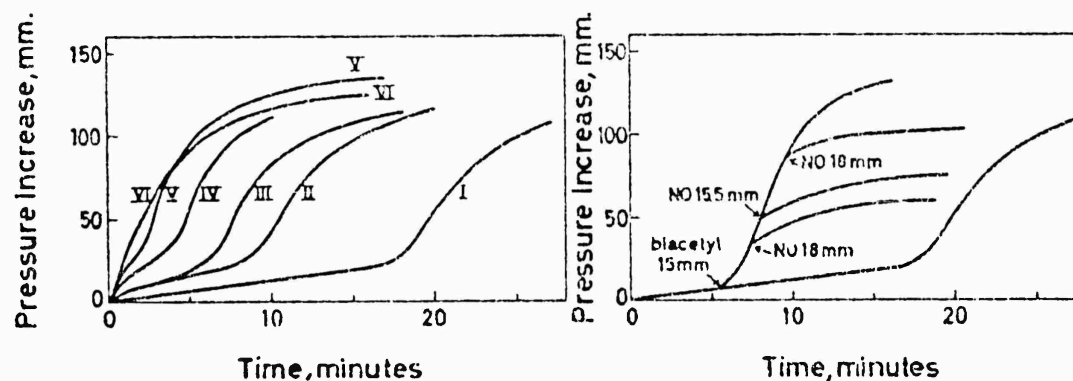


Fig. 15. 520°C. Initial pressures, methylal 75 mm, nitric oxide 5 mm, biacetyl, curves I - 0; II - 4; III - 6.5; IV - 8.2; V - 15 mm

Fig. 16. 520°C. Effect of nitric oxide upon the biacetyl sensitized reaction. Initial pressures, methylal 75 mm, nitric oxide 5 mm with a further addition of biacetyl 15 mm at 5' 30"

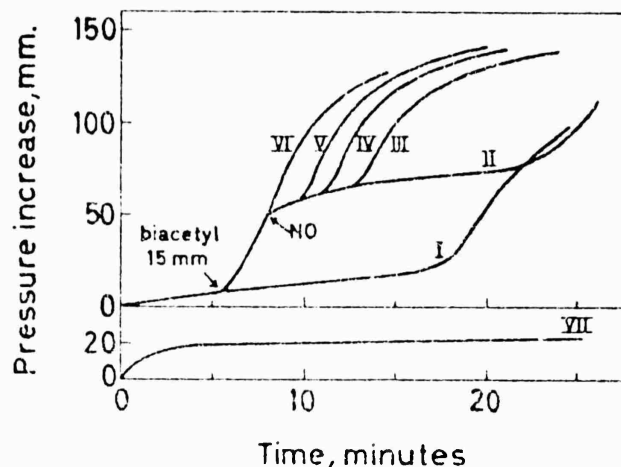


Fig. 17. 520 °C. Initial pressures, methylal 75 mm, nitric oxide 5 mm. Curve I without further additions. Curves II, III, IV, V, VI with a further addition of biacetyl 15 mm and 14.5 - 11.5 - 10 - 10 - 0 mm of a further nitric oxide addition. Curve VII, decomposition of 15 mm biacetyl.

The results obtained if addition of increasing amounts of biacetyl is made at a fixed reaction time (5' 30") to the methylal (75 mm) and nitric oxide (5 mm) decomposing mixture are plotted in fig. 14. A similar effect is obtained if both a fixed amount of nitric oxide (5 mm) and increasing biacetyl amounts are added at zero reaction time (fig. 15).

Figures 13, 14 and 15 seem to prove that biacetyl acting upon the inhibited methylal decomposition may sensitize a reaction. Fig. 16 and 17 show that the sensitized reaction may again be suddenly inhibited if nitric oxide is added. Moreover, the inhibition time increases with the NO pressure of the latter addition, when the other experimental conditions remain unchanged.

The above results may be explained in one of the two following ways: either biacetyl can start some nitric oxide uninhabitable methylal chains or it reacts with nitric oxide, the assumed sensitization being only a suppression of inhibition owing to the consumption of nitric oxide, due to the biacetyl added.

The latter of the above possibilities seemed to be excluded owing to the already mentioned results (6) of previous investigators. However, some experiments made by us in order to find out the possible effect of nitric oxide upon biacetyl seem to show that there is a reaction between them, a

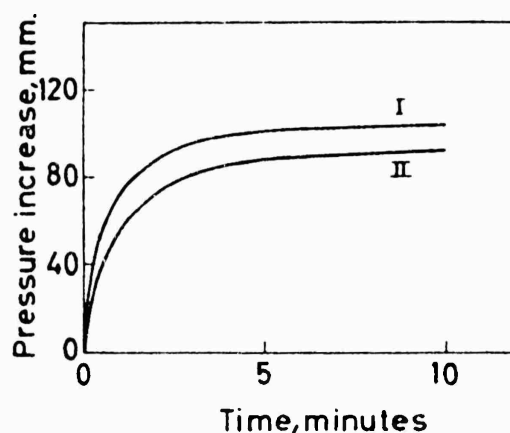


Fig. 18. 520°C. Curve I, 75 mm biacetyl. Curve II, 75 mm biacetyl plus 70 mm nitric oxide

decrease in the Δp -time curves being observed at great NO/biacetyl ratios (fig. 18). Similar results have been obtained at higher methylal pressures (150 mm).

III.3.2. Analyses

Some infrared spectrometry analyses have been undertaken in order to study the possibility of nitric oxide reacting with biacetyl.

Qualitative analyses of the products formed from 75 mm biacetyl plus 50 mm nitric oxide after 14 minutes reaction time at 520°C show that an appreciable amount of hydrogen cyanide (about 10 mm) is formed. Moreover we have detected several bands around 2300 cm^{-1} and carefully measured their frequencies which correspond to one (or more than one) product whose identity has not as yet been established.

Quantitative analyses of the products obtained from 30 mm biacetyl and 10 mm nitric oxide for several reaction times have also been made (table V, fig. 19). The optical densities which correspond to the unknown product have been plotted under the heading "nitrile" because most nitriles are absorbent in the vicinity of 2300 cm^{-1} and the possibility of one product being a nitrile cannot be ruled out.

We have carried out several analyses for different reaction times corresponding to the decomposition of 75 mm initial pressure methylal inhibited by 5 mm nitric oxide with a further addition of biacetyl at 5'30". The results are shown in table VI and fig. 20. The differences we have found between the pressures measured on the manometer and the

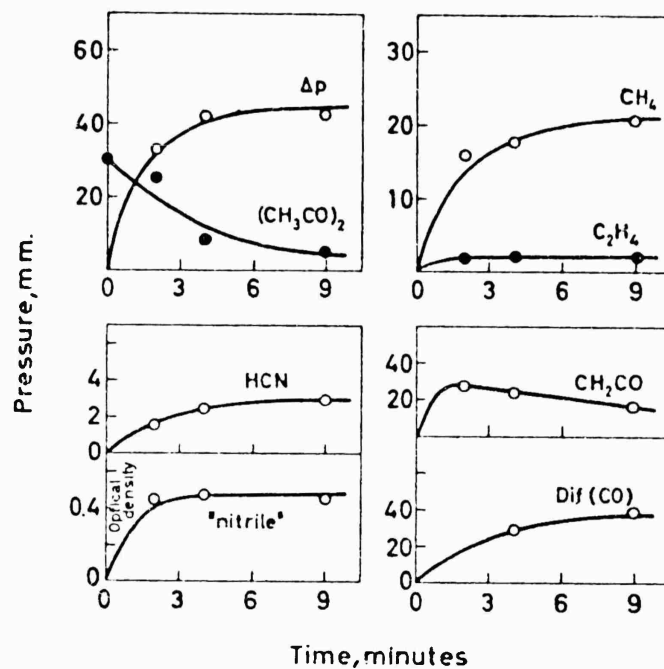


Fig. 19. 520°C. 30 mm biacetyl, 10 mm nitric oxide

TABLE V

Nitric oxide inhibited biacetyl decomposition at 520°C
Initial biacetyl pressure 30 mm; Initial nitric oxide
pressure 10 mm (pressures in mm)

Reaction time (minutes)	Biacetyl	Methane	Ketene (~)	Ethylene	Hydrogen cyanide	"Nitrile" (optical density)	Dif. (carbon monoxide)	Total pressure (sampling)
2	25	16	28	1.8	1.6	0.445		73
4	8	17.5	24.5	2	2.3	0.478	29.5	82
9	5	20.5	17	2.1	2.9	0.445	38.5	82

sum of the partial pressures analysed in the volatile fraction at liquid air temperature should be ascribed to molecular hydrogen formed in the reaction. Similar small differences have also been found in the medium fraction, between liquid air and solid CO₂ temperatures. They are probably due to small amounts of ethane being present among the products. Ethane is not detectable by infrared spectrometry owing to its small absorbing power under the experimental conditions of these analyses.

TABLE VI

Nitric oxide inhibited biacetyl sensitized methylal decomposition at 520°C
Initial methylal pressure 75 mm; initial nitric oxide pressure, 5 mm; biacetyl
15 mm added at 5'30" (pressures in mm)

Exp	Reaction time (minutes)	Methylal	Biacetyl	Methane	Carbon monoxide	Methyl formate	Methyl alcohol	Hydrogen cyanide	Ketene	"Nitrile" (optical density)	Dif. (vol)	Dif. (cond)	Total pressure (sampling)
1	5'30"	66	15	6	5.5		2	0.15				2	101
2	5'30"	66	15	5.5	2.5		3	0.08			7	3.4	102.5
3	8'10"	41		19	22	12.5	1.5	0.05	1		40	2.5	143
4	12'15"	28		28.5	26	13.5	3.5	0.31	0.5		67	7	184
5	16'15"	17		48	47.5	15	1.5	0.48			81	8.5	226.5
6	17'45"	23		56	48.5	14	1	0.40			83	3	232.5
7	20'	22		45	48	15.5	3	0.32		0.12	81.5	11	230
8	19'	14.5		46	46.5	15	2	0.30		0.09	76	18	225
9	22'	23.5		39.5	39.5	14	2.5	0.50		0.19	86	10	224
10	20'	19		46	46	18.5	6.5	0.63		0.16			236
11	10'	25	8	48.5		21	5	0.47		0.26			197
12	18'	33	10.5	63		14	6.5	0.64		0.29			242.5

Note: Experiments 1 to 7 have been made fractionating at liquid air temperature; experiments 8 and 9 at liquid air and solid CO₂ temperatures; experiments 10, 11 and 12 by directly sampling.

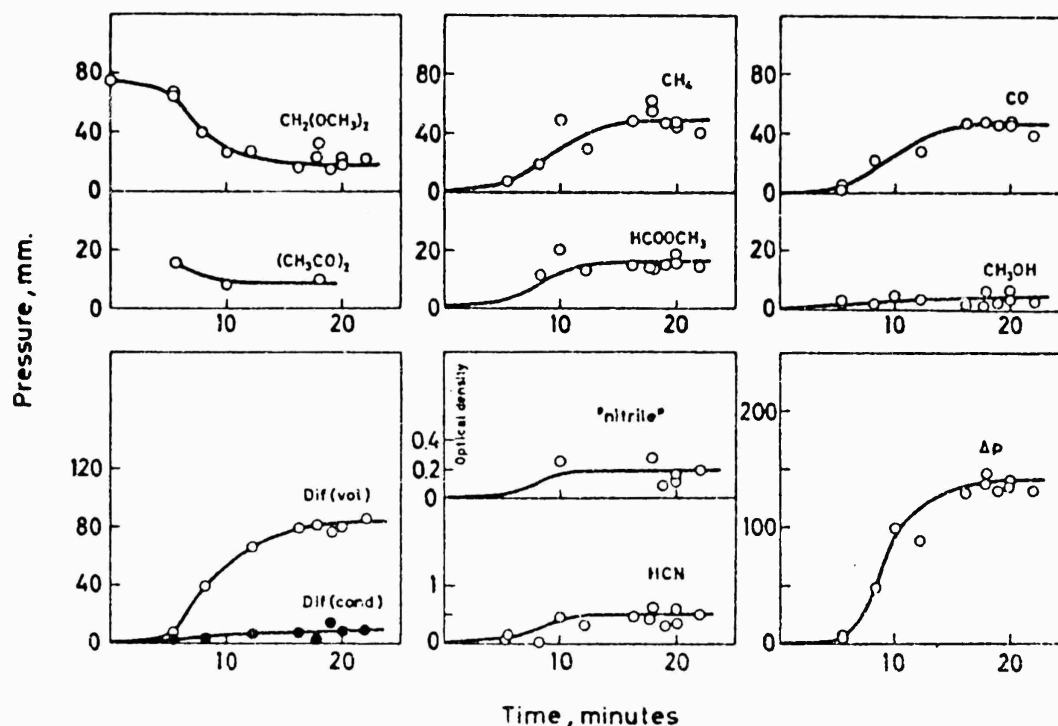


Fig. 20

III.4. Di-*t*-butyl peroxide

Experiments on the influence of di-*tert*-butyl peroxide as a possible sensitizer of methylal decomposition have been made in a large temperature range (168.5 - 527°C).

At first sight the pressure increase-time plots obtained for the higher temperatures (527 and 505°C) with 75 mm starting methylal pressure and several D.B.P. pressures up to 50 mm, showed a rate decrease for increasing D.B.P. pressures which, on closer examination, was shown to be due to the high decomposition rate of D.B.P. at these temperatures. There is a very quick increase in pressure before the total amount of methylal and D.B.P. mixture has reached the reaction vessel and, consequently, the apparent initial pressure inside the reaction vessel actually corresponds to a methylal poor mixture owing to the considerable amount of decomposition products present. The measured rate is then lower in the presence of D.B.P.

Experiments have been carried out at lower temperatures (423, 416, 401 and 316°C) where the normal methylal decomposition is not detec-

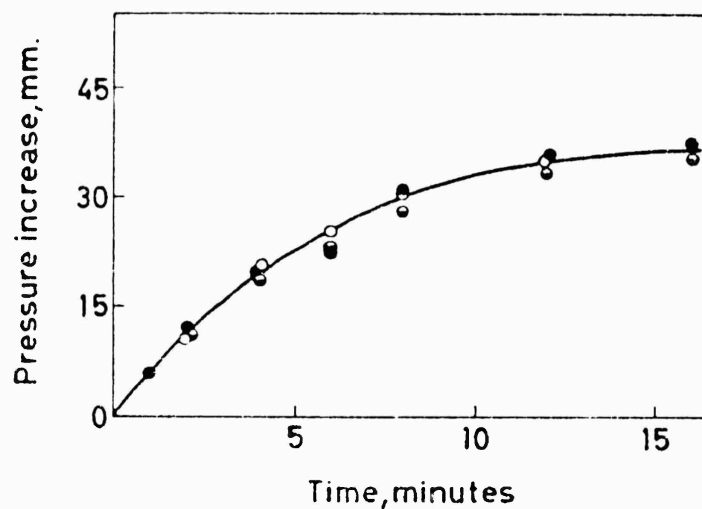


Fig. 21. 185°C. ● ○ 75 mm methylal, 28 mm di-t-butyl peroxide. ● - 28 mm di-t-butyl peroxide

table, but here again is not possible to study the sensitization which is due, once more, to the fact that D.B.P. decomposes too quickly.

At still lower temperatures (185 - 168.5°C) where D.B.P. decomposes at a measurable rate, it has been proved that it exerts no sensitizing effect on methylal decomposition (Fig. 21). The methylal chain transmission rate is probably very low at these temperatures and no chain would be formed even if some attack of the D.B.P. derived radicals on the methylal molecules were to take place.

IV. STUDY OF THE NITRIC OXIDE INHIBITED METHYLAL DECOMPOSITION

IV.1. Discussion of the hypothetical mechanisms of inhibition

As we have mentioned before (1) (5), a general feature of the NO inhibited decomposition of organic compounds seems to be that the reaction is not completely suppressed by the inhibitor, and a minimum rate differing from zero is reached as the NO concentration increases. Whether the remaining reaction is a chain-free molecular process or whether it corresponds to a fixed state of incomplete chain suppression has been the matter of much controversy (6) (7) (8) (9) (10) (11) (12) (13) (14) (15). Summarizing the results found in literature, it seems probable that frequently maximum nitric oxide inhibition does not correspond to the complete suppression of chain processes, although the possibility of a simultaneous rearrangement reaction is not excluded. However, the similarity of the results obtained with propylene and nitric oxide in previous investigations where the same inhibition limit appeared to have been reached with both inhibitors has been given great weight, as seeming to indicate complete suppression of chains.

The latter explanation may not be safely accepted in the decomposition of methylal where considerable differences have been found for both inhibitors, nitric oxide or olefine (5). Moreover, the stoichiometry of nitric oxide inhibited methylal decomposition could not be explained in terms of only one rearrangement process, but rather in those of at least three independent rearrangement processes.

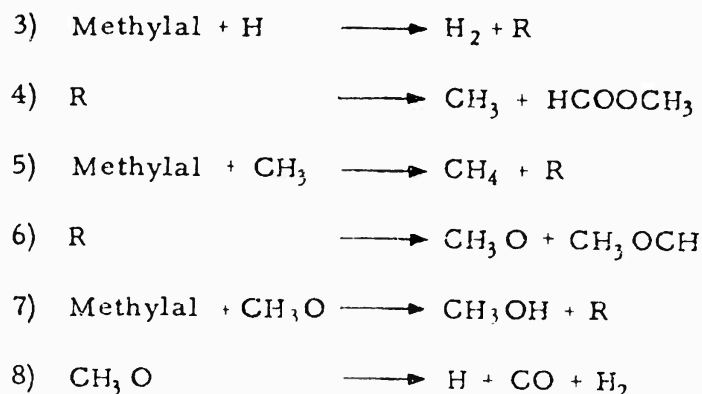
These considerations led us immediately to suspect that methylal decomposition may well be an example of an instance of the non-disappearance of chain processes in the presence of nitric oxide. Consequently, we decided on a detailed discussion of the experimental results found in this research with the aim of establishing whether they could all be explained without assuming that the "completely" inhibited reaction is wholly or in part a rearrangement process.

The chain sequence for the normal methylal decomposition was:

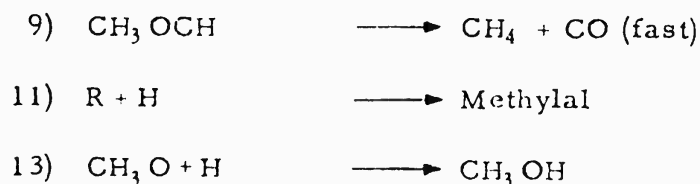
Initiation.



Propagation.



Breaking.



(R stands for the radical $\text{CH}_3 \text{OCHOCH}_3$)

where steps 10) and 12) were already neglected in the mathematical treatment of the normal methylal decomposition (5).

In the above chain sequence there are several carrier radicals. If we assume that NO reacts at comparable rates with all the different radicals, the chain process would be completely suppressed and, as normal methylal chains are rather long, in the presence of sufficient NO concentration the rate should be reduced several hundredfold. This is not corroborated by experiment and, consequently, a residual chain process could not be explained in this way. The next step is to assume that several of the different radicals may be considered as practically eliminated in the reaction with NO and that a residual chain process is carried on by the radicals whose reaction with NO is negligible. In that which follows several possibilities are considered and the further implications of applying the steady state approximation to the mechanisms that result, are described.

It is well known that many thermal decompositions of organic compounds are explained in terms of those mechanisms where large and small radicals are alternate carriers of the chain, larger radicals decomposing into smaller ones and products and the smaller reacting by a metathetical reaction. It has been already suggested (16) that in the thermal decomposition of diethyl ether, inhibition may be due to the fact that nitric oxide reacts mainly with the large radicals.

1) Nitric oxide reacts with the R radical

The mechanism of the inhibited reaction would consist of steps 1), 2), 3), 5) and:



With such a chain sequence, methyl alcohol and carbon monoxide should disappear from among the products. The experimental results prove that the contrary happens and, therefore, that the mechanism may be ruled out. However the possibility remains that two different large radicals are formed in normal decomposition, and that nitric oxide reacts preferentially with only one of them.

2) There are two large radicals, nitric oxide reacting mostly with one of them

Decomposition by steps 4) and 6) would correspond to each of two different large radicals which might be $\text{CH}_3\text{OCHOCH}_3$ and $\text{CH}_2\text{OCH}_2\text{OCH}_3$ formed according to two different possibilities of radical attack on the methylal molecule. Nitric oxide inhibition would be attributable to reaction with only one of these two large radicals.

If it is assumed that $R_1 + NO \longrightarrow \text{products}$, steps 4) and 11) would disappear and the methyl formate formation rate in the inhibited reaction would be reduced to $k_1 M$, a fact which was not proved correct by experiment. If, on the other hand, we assume that $R_2 + NO \longrightarrow \text{products}$, steps 6) and 11) would be suppressed and the steady state approximation for the inhibited reaction would lead to

$$[\text{CH}_4] = [M]_0 \quad [M] = [\text{HCOOCH}_3]$$

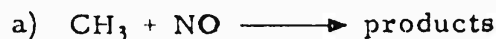
which is not correct from the experimental point of view.

It is worth mentioning here that both this and several other modifications of this mechanism have been checked with experimental results

without any success and, consequently, in the following proposed mechanisms we will only discuss the action of nitric oxide on the small radicals.

3) Nitric oxide reacts mostly with methyl radicals

In the normal decomposition mechanism step 5) would be substituted by:



Here again, the stoichiometric relationships:

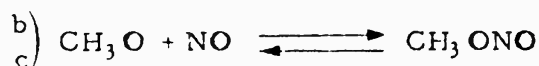
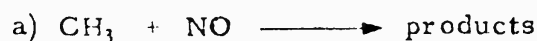
$$[\text{CO}] + [\text{CH}_3\text{OH}] = 2 [\text{CH}_4]$$

$$[\text{HCOOCH}_3] + [\text{CH}_4] + [\text{M}] = [\text{M}]_0$$

which are derived from the steady state approximation when applied to this mechanism, are experimentally proved wrong.

4) Nitric oxide reacts with the methyl radicals and partially with the methoxyl radicals

Step 5) could be neglected as in mechanism 3). The following steps should be added:



The possibility of alkoxyl radicals reacting with nitric oxide is supported by recent research work (17). However, it seems that organic nitrites produce nitric oxide readily and that the opposite reaction is not so easy (2). In consequence, it is to be expected that equilibrium

b)
c) will shift rather markedly towards the left.

Moreover, the steady state approximation would give;

$$\left[M \right]_0 - \left[M \right] = \left[CH_4 \right] + \left[HCOOCH_3 \right]$$

which renders the mechanism inadequate for experimental results.

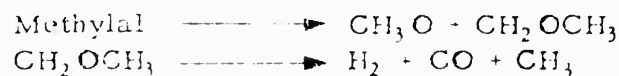
If k_b were much smaller than k_c , k_a and k_{13} , the results obtained

with this mechanism would be equivalent to those obtained with mechanism 3).

5) Nitric oxide reacts with the methyl radicals and with the hydrogen atoms

If nitric oxide were to react with practically all methyl radicals and hydrogen atoms, the whole methylal chain would be suppressed and the rate would be much more smaller than found.

In consequence, the possibility of a different type of chain initiation, such as:



is to be considered together with the above conditions. At "complete" inhibition, the reaction would then proceed through a chain mechanism, but the difficulty is that the steady state approximation leads to:

$$\left[M \right]_0 - \left[M \right] = \left[CH_3OH \right] = \left[CH_4 \right] + \left[HCOOCH_3 \right]$$

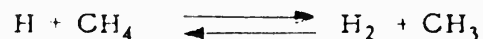
which is far from fitting in with experimental results.

A possible alternate explanation might be that nitric oxide does not react with all the methyl radicals and hydrogen atoms present. The process might be rather considered as a competitive reaction between methylal, nitric oxide and these active intermediates. Perhaps the rate constant of step 5) is greater than that of step 3) and, consequently, in normal decomposition hydrogen atom concentration is higher than methyl radical concentration. Nitric oxide would therefore react at a larger rate with the former than with the latter.

On the basis of this or of a similar hypothesis it would not be difficult to explain an almost constant inhibition limit, where the residual chain process would be transmitted by the methyl, methoxyl and R radicals. After the major part of the reaction was inhibited by nitric oxide we should only expect a slight decrease in rate for greater NO concentrations. However, it is unfortunate that such a mechanism does not seem

acceptable, due to the fact that it has been found experimentally that instead of diminishing, the rate increases for higher NO concentrations.

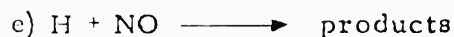
So far it is of interest that if the equilibrium:



is taken into account, the results obtained are equivalent to the above, because this equilibrium is mathematically implied in the equation already considered for the normal decomposition mechanism.

6) Nitric oxide reacts with the hydrogen atoms

Step 3) might be neglected and:



should account for the inhibition process.

The fact that hydrogen atoms and nitric oxide react with each other has been reported by Taylor and Tanford (18). Moreover the percentage of molecular hydrogen found in the present research is lower for the reaction mixtures obtained in the nitric oxide inhibited methylal decomposition than in those obtained in uninhibited decomposition. In view of these considerations, it would not be unlikely that step e) were of some importance in the inhibition process.

By application of the steady state approximation, the following stoichiometric relationships are derived for inhibited decomposition:

$$\begin{aligned} [\text{CO}] + [\text{HCOOCH}_3] &= [\text{CH}_4] + [\text{H}_2] \\ [\text{M}]_0 - [\text{M}] &= [\text{CH}_4] \end{aligned}$$

These equalities are not in large disagreement with experiment but utilisation of this mechanism is unable to explain some experimental details of the reaction rate-nitric oxide plots and the products formed from nitric oxide offer stoichiometric difficulties.

IV.2. The proposed mechanism

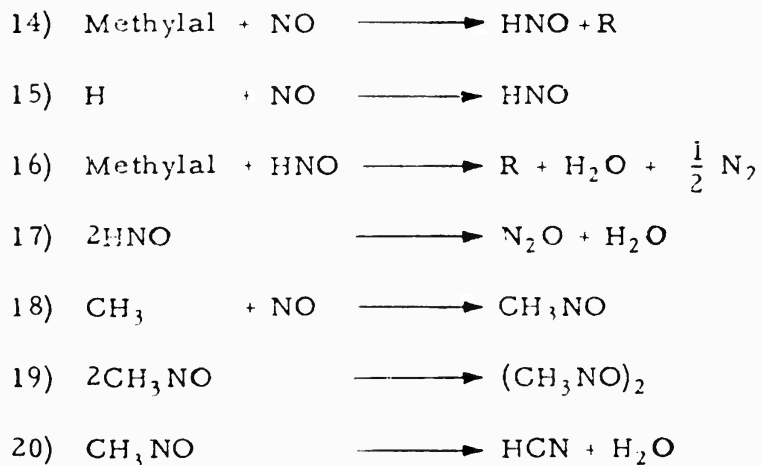
A quick review of our attempts in the above mentioned search for a suitable set of steps reveals that none of the proposed mechanisms satisfactorily explains how nitric oxide reacts during the inhibition process. According to the experimental results already obtained (5), it appears

unequivocal that nitric oxide is exhaustively consumed during the inhibition process in methylal decomposition. It was also concluded that very likely the normal methylal chains are several hundred steps long. Then, if nitric oxide is used up in the reaction with the radicals produced in the chain initiation process, it is impossible to explain its comparatively high rate of consumption in terms of any of the above mechanisms. This difficulty still remains if the residual reaction at "complete" inhibition was assumed to be mainly a rearrangement process.

The above ideas suggest that the greater part of nitric oxide may be consumed in a process other than inhibition. This process should be a chain. The difficulty of fitting experimental results to the partially inhibited chain hypothesis has been proved in the preceeding discussion. Therefore, in the following, the possibility of a new chain initiated by nitric oxide reacting as a radical, will be considered.

The mechanism proposed must be also able to explain: a) the stoichiometry of the reaction; b) the dependence of the rate on the variations experienced by the nitric oxide pressure-methylal pressure ratios; c) the dependence of rate on the methylal pressure for a fixed nitric oxide to methylal ratio; d) the production of HCN.

Taking into account all these conditions, we propose a mechanism formed by the chain sequence from steps 1) to 13) in page 24 together with the following:



Several attempts to explain experimental results by considering only some of these steps 14) to 20) have been unsuccessful.

As the R radicals are comparatively large, it is likely that they decompose before they react and, therefore, the action of nitric oxide upon them, if any, would be unimportant and has been neglected. As we

pointed out before, the $\frac{b}{c}$ equilibrium between CH_3O and NO is probably

shifted towards the left and has been also neglected. Although steps 16) and 17) may be considered as speculative, they are not without foundation considering the results obtained in previous investigations (18) (19) (20). Moreover, Coe and Doumani (21) have isolated the $(\text{CH}_3\text{NO})_2$ dimer.

IV.2.1. The stoichiometry of the inhibited reaction

The atom balance between reactants (methylal and nitric oxide) and products forms according to the proposed mechanism leads to a set of four independent equations to which a fifth one, arising from the mechanism, may be added. In a simplified form, the five independent equations may be written as follows:

$$[\text{H}_2\text{O}] = [\text{HCN}] + 2 [\text{N}_2] + [\text{N}_2\text{O}] \quad [1]$$

$$[\text{M}]_0 - [\text{M}] = [\text{CH}_4] + [\text{HCN}] + 2 [(\text{CH}_3\text{NO})_2] \quad [2]$$

$$[\text{NO}]_0 - [\text{NO}] = 2 [(\text{CH}_3\text{NO})_2] + [\text{N}_2\text{O}] + [\text{H}_2\text{O}] \quad [3]$$

$$[\text{M}]_0 - [\text{M}] = [\text{HCCOCH}_3] + \frac{1}{2} [\text{CO}] + \frac{1}{2} [\text{CH}_3\text{OH}] \quad [4]$$

$$[\text{CH}_3\text{OH}] + [\text{H}_2] + [\text{H}_2\text{O}] = [\text{CO}] + [(\text{CH}_3\text{NO})_2] + \frac{3}{2} [\text{HCN}] \quad [5]$$

The validity of these equations has been checked successfully with the experimental results of the inhibited reaction at 559°C (Table III, ref. (5)). Methyl formate partially decomposes at this temperature and therefore, the amount of CO_2 produced has been added to that of methyl formate and subtracted from the amount of methane found by analysis.

It is worth mentioning that equation [2] proves that

$$[\text{M}]_0 - [\text{M}] > [\text{CH}_4]$$

which is a different conclusion than that reached for the uninhibited reaction, where the amount of consumed methylal was equal to that of produced methane.

IV.2.2. The steady state approximation

The steady state approximation requires:

$$k_1 M - k_5 MA + k_4 R - k_{18} AN = 0 \quad [6]$$

$$- k_7 MB + k_6 R - k_8 B - k_{13} HB = 0 \quad [7]$$

$$k_1 M - k_3 MH + k_8 B - k_{11} RH - k_{13} HB - k_{15} HN = 0 \quad [8]$$

$$k_3 MH + k_5 MA + k_7 MB - (k_4 + k_6) R - k_{11} RH + \\ + k_{16} M [HNO] + k_{14} MN = 0 \quad [9]$$

$$k_{15} HN - k_{16} M [HNO] - 2k_{17} [HNO]^2 + k_{14} MN = 0 \quad [10]$$

$$k_{18} AN - 2k_{19} [CH_3 NO]^2 - k_{20} [CH_3 NO] = 0 \quad [10 \text{ bis}]$$

where M, H, A, B, R and N stand for the concentrations of methylal, hydrogen atoms, methyl, methoxyl, R radicals and nitric oxide, respectively.

Two independent expressions for $\frac{R}{M}$ may be derived from the preceding:

$$2k_3 H - \frac{k_1 k_{18} N}{k_5 M + k_{18} N} + k_{14} N + k_{15} H \frac{N}{M} + k_{16} [HNO] = \\ = \left(\frac{2k_6 k_8}{k_7 M + k_8 + k_{13} H} + \frac{k_{18} k_4 N}{k_5 M + k_{18} N} \right) \frac{R}{M} \quad [11]$$

and:

$$k_1 + \frac{k_1}{k_{18} N} - k_{15} H \frac{N}{M} + k_{14} N + k_{16} \left[\text{HNO} \right] =$$

$$1 + \frac{1}{k_5 M}$$

$$= \left(\frac{2k_6 k_{13} H}{k_7 M + k_8 + k_{13} H} + 2k_{11} H + \frac{k_4 k_{18} N}{k_5 M + k_{18} N} \right) \frac{R}{M} \quad [12]$$

if $N = O$, equations [11] and [12] reduce to [5] and [6] of the normal decomposition treatment (5).

Here again the general expression relating H and M , which may be derived from [11] and [12], is very complicated and cannot be solved for H . However, several relationships may be obtained which will constitute the basis for checking the validity of the proposed mechanism.

Taking into account equation [9], the rate of methylal consumption may be expressed by:

$$- \frac{dM}{dt} = k_1 M - [k_4 + k_6] R \quad [13]$$

which is formally the same as the corresponding equation in the uninhibited reaction treatment (5). However, here methylal is consumed at a smaller rate because the R concentration is lower, although no appreciable reaction between the R radicals themselves and nitric oxide was expected to take place considering the mechanism under discussion.

The rate of nitric oxide consumption may be:

$$- \frac{dN}{dt} = k_{15} HN + k_{18} AN + k_{14} MN \quad [14]$$

The building up rates of the products formed in the inhibited reaction,

If we take [6] and [7] into account, are:

$$\frac{d [\text{CH}_4]}{dt} = \frac{k_1 M}{1 + \frac{k_{18} N}{k_5 M}} + \left(k_6 + \frac{k_4}{1 + \frac{k_{18} N}{k_5 M}} \right) R \quad [15]$$

$$\frac{d [\text{CO}]}{dt} = k_6 R \left(1 + \frac{k_8}{k_8 + k_7 M + k_{13} H} \right) \quad [16]$$

$$\frac{d [\text{HCOOCH}_3]}{dt} = k_1 M + k_4 R \quad [17]$$

$$\frac{d [\text{H}_2]}{dt} = k_3 M H + \frac{k_6 k_8 R}{k_7 M + k_8 + k_{13} H} \quad [18]$$

$$\frac{d [\text{CH}_3\text{OH}]}{dt} = k_6 R \left(1 - \frac{k_8}{k_7 M + k_8 + k_{13} H} \right) \quad [19]$$

$$\frac{d [\text{N}_2]}{dt} = \frac{1}{2} k_{16} M [\text{HNO}] \quad [20]$$

$$\frac{d [\text{HCN}]}{dt} = k_{20} [\text{CH}_3\text{NO}] \quad [21]$$

$$\frac{d [\text{N}_2\text{O}]}{dt} = k_{17} [\text{HNO}]^2 \quad [22]$$

$$\frac{d [\text{H}_2\text{O}]}{dt} = k_{16} M [\text{HNO}] + k_{17} [\text{HNO}]^2 + k_{20} [\text{CH}_3\text{NO}] \quad [23]$$

$$\frac{d [(\text{CH}_3\text{NO})_2]}{dt} = k_{19} [\text{CH}_3\text{NO}]^2 \quad [24]$$

IV.2.3. Relationships among the elementary rate constants and the rates

Relationships similar to those obtained in the uninhibited reaction treatment may be derived.

From [16] and [18]:

$$k_3 H = V_{H_2} - \frac{1}{2} (V_{CO} - V_{CH_3OH}) \quad [25]$$

From [16] and [19]:

$$k_6 R = \frac{M}{2} (V_{CO} + V_{CH_3OH}) \quad [26]$$

From [17] and [26]:

$$\frac{k_6}{k_4} = \frac{V_{CO} + V_{CH_3OH}}{2 V_{HCOOCH_3} - 2k_1} \quad [27]$$

where the V's stand for the corresponding rates divided by M.

The last three equations correspond to [32], [33] and [27] respectively, in the normal decomposition treatment (5). They are of interest because the values of $k_3 H$, $k_6 R$ and k_6/k_4 would be obtainable if sufficiently accurate experimental data were available. Unfortunately, the analytical results of the inhibited reaction at suitable temperatures, such as 559°C, are not sufficiently accurate to allow such a precise measurement as would be desirable of the production rates along the reaction and only a rough calculation could be made.

Two equations corresponding to [28] and [29] of the normal decomposition treatment have been obtained and from them, the following inequalities may be derived:

$$\frac{k_7}{k_8} + \frac{1}{M(V_{CO} - V_{CH_3OH})} \left[k_1 \left(1 + \frac{1}{1 + \frac{k_{18} N}{k_5 M}} \right) + 2k_{14} N \right] > \frac{2V_{CH_3OH}}{M(V_{CO} - V_{CH_3OH})} > \frac{k_7}{k_8} \quad [28]$$

which reduce to [30] of the normal decomposition mechanism (5) if the amount of nitric oxide is equated to zero.

The left hand side of inequalities [28] increases with nitric oxide concentration and, consequently, the usefulness of [28] in the inhibited reaction treatment lies only in that it fixes a higher limit for the k_7/k_8 value.

IV.2.4. The pressure increase rate and the lack of inhibition limit

A large number of experiments (about two hundred) have been carried out at the temperatures of 513, 520, 530 and 559°C in order to establish in detail the influence of nitric oxide on the methylal decomposition pressure increase rate. The best curves that may be drawn through the experimental clouds of points at the four temperatures have been plotted in fig. 22. According to these results, there is no inhibition limit, the curves showing a minimum in rate which at the lower temperatures considered appears to be sharper and tends to be displaced towards low nitric oxide pressures. The curves exhibit a sharp increase in rate following the minimum as the nitric oxide pressure increases and a smooth increase at still greater nitric oxide pressures.

Experiments were carried out with 150 mm initial pressure methylal and 14 mm nitric oxide pressure at 520°C with the addition of increasing amounts of nitrogen to find out whether the smooth increase of the curves in fig. 22 could be due to some third body effect produced by nitric oxide, or otherwise. The results plotted in fig. 23 show that the influence on the reaction of N_2 as a third body is comparatively negligible and that it may be safely assumed that nitric oxide actually reacts with methylal.

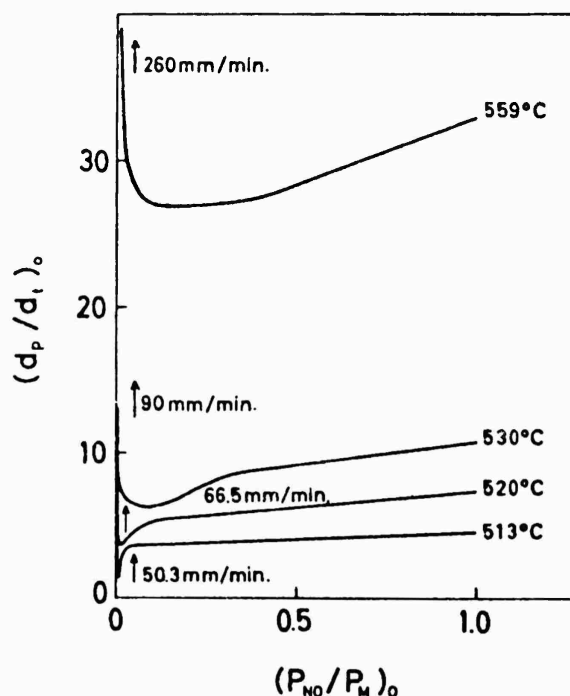


Fig. 22

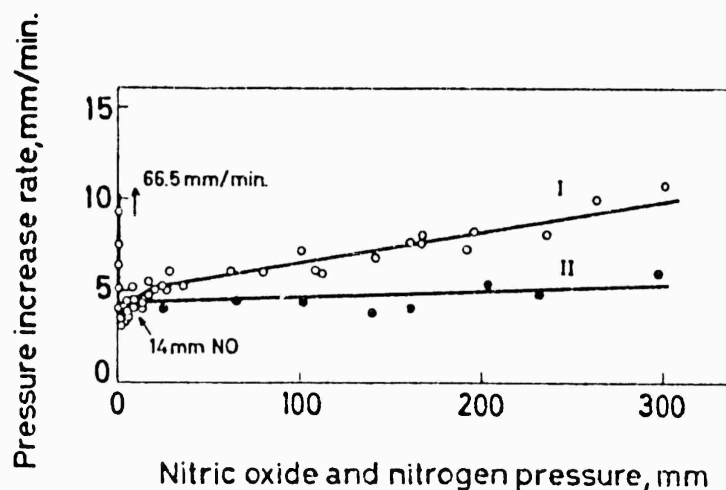


Fig. 23. 520°C. Curve I - 150 mm methylal with nitric oxide additions. Curve II - 150 mm methylal plus 14 mm nitric oxide with nitrogen additions

Equation [13] gives the methylal consumption rate in terms of the R radicals concentration. In order to establish the character of its dependence on the NO pressure, it is convenient to derive an expression of R depending on the NO pressure.

From equations [6] [7] and [9]:

$$R = \frac{1}{k_4 + k_6 + k_{11} H} \left[k_3 M H + k_5 M \frac{k_1 M + k_4 R}{k_5 M + k_{10} N} + k_7 M \frac{k_6 R}{k_7 M + k_8 + k_{13} H} + k_{16} M [HNO] + k_{14} MN \right] \quad [29]$$

In this expression, the terms $k_{11} H$ and $k_{13} H$ which form part of two sums together with others independent of the NO pressure, become very small during the inhibition process and may be neglected in the benefit of simplification [29]. However, no extrapolation at zero nitric oxide pressure will be allowed to make, because the conclusions arrived at would be wrong owing to the absence of these chain terminating terms. But the simplification holds, provided no such extrapolation was made.

From [7], [8] and [29]:

$$R (k_4 + k_6) = \frac{k_3 M}{k_3 M + k_{15} N} \left(k_1 M + \frac{k_6 k_8 R}{k_7 M + k_8} \right) + k_5 M \frac{k_1 M + k_4 R}{k_5 M + k_{18} N} + \frac{k_7 M k_6 R}{k_7 M + k_8} + k_{16} M [HNO] + k_{14} MN \quad [30]$$

The [HNO] value in equation [30] may be written in an explicit form employing equation [10]. It is found experimentally that for small NO pressures, the rate decreases steeply with a parallel decrease in the H concentration. Consequently, the k_{15} HN term may be neglected in [10] and the following approximate expression obtained:

$$[HNO] \approx \frac{k_{16} M}{4k_{17}} \left(-1 + \sqrt{1 + \frac{8k_{14} k_{17} N}{k_{16}^2 M}} \right) \quad [31]$$

From [30] and [31] we may derive an expression of R in terms of M and N which, together with [13], allows $\frac{dM}{dt}$ to be expressed in terms of these variables. However, such an equation would not be of the adequate form to check experimental results due to the fact that the methylal consumption rate measurements are not accurate enough. Consequently, it was considered worth while to find an equation which relates the dp/dt and N/M values considering that much more accurate measurements can be made on the Δp -time curves.

The pressure increase (Δp) may be written as a difference between the products formed and consumed. Considering the stoichiometric relationships [1] [2] [3] and [5], this difference may be transformed into the more convenient form:

$$\Delta p = [HCOOCH_3] + 2 [CO] - [N_2] - \frac{3}{2} ([M]_0 - [M]) + \frac{3}{2} [CH_4] + 2 [HCN] - [N_2O] \quad [32]$$

An equation for dp/dt may be obtained from [32] if we employ [13] [15] [16] [17] and [20]:

$$\begin{aligned} \frac{dp}{dt} = & \left[-\frac{1}{2} k_4 + \frac{3}{2} \frac{k_4}{1 + \frac{k_{18} N}{k_5 M}} + 2k_6 + 2 \frac{k_6 k_8}{k_8 + k_7 M} \right] R + \\ & + \left[-\frac{1}{2} k_1 + \frac{3}{2} \frac{k_1}{1 + \frac{k_{18} N}{k_5 M}} \right] M - \frac{1}{2} k_{16} M [\text{HNO}] \quad [33] \end{aligned}$$

where the difference $2 \frac{d[\text{HCN}]}{dt} - \frac{d[\text{N}_2\text{O}]}{dt}$ has been neglected because each of these two rates is small if compared with the other ones in [33], and their difference is still smaller.

Eliminating R and [HNO] from [30] [31] and [33] we obtain the following:

$$\begin{aligned} \frac{dp}{dt} = & k_1 M \left(\frac{3}{2} n_A - \frac{1}{2} \right) - k_{14} M n_{\text{HNO}} + \\ & + \left[(n_{\text{II}} + n_A) k_1 M + (1 + 2n_{\text{HNO}}) k_{14} M N \right] \frac{\frac{3}{2} n_A - \frac{1}{2} + 2(1 + m_B) \frac{k_6}{k_4}}{1 - n_A + m_B (1 - n_{\text{II}}) \frac{k_6}{k_4}} \quad [34] \end{aligned}$$

where:

$$n_A = \left(1 + \frac{k_{18} N}{k_5 M} \right)^{-1}; \quad n_{\text{II}} = \left(1 + \frac{k_{15} N}{k_3 M} \right)^{-1};$$

$$n_{\text{HNO}} = \left(1 + \sqrt{1 + \frac{8k_{14} k_{17} N}{k_{16}^2 M}} \right)^{-1}; \quad m_B = \left(1 + \frac{k_7 M}{k_8} \right)^{-1}$$

The parameters involved in equation [34] may be numerically reduced to seven which, if conveniently selected, are:

$$k_{15}/k_3, \quad k_{18}/k_5, \quad k_6/k_4, \quad k_7/k_8, \quad k_{17}/k_{16}^2, \quad k_1 \text{ and } k_{14}.$$

The trial and error method has been repeatedly applied to equation [34] in order to find the more suitable values of the parameters which permit this equation to fit with the experimental results obtained in this research.

Values obtained for 559, 530, 520 and 513°C are in table VII. The corresponding curves of the $(dp/dt)_0$ versus $(N/M)_0$ values have been calculated for the four temperatures employing the parameters obtained, and are plotted in fig. 24. It may be observed that the adjustment of these theoretical curves to the experimental points in fig. 24 is very acceptable indeed for all the temperatures concerned.

TABLE VII

Temperature °C	k_{15}/k_3	$\frac{k_{18}}{k_5}$	$\frac{k_{14} k_{17}}{k_{16}^2}$	k_6/k_4	k_7/k_8	k_1	k_{14}
559	500	2	0.25	0.35	0.00111	0.0185	0.00073
530	500	3	0.75	0.355	0.0028	0.0030	0.00034
520	1000	5	1.25	0.30	0.00333	0.0016	0.00039
513	1000	5	1.25	0.22	0.00148	0.00043	0.00037
459				1	0.0025	(0.00006)	-
<p>Notes: The values for 459°C have been calculated from the data obtained for the uninhibited methylal decomposition. Monomolecular rate constants are in min^{-1}, bimolecular rate constants in $\text{mm}^{-1} \text{min}^{-1}$.</p>							

It is worth remarking that there is no relation whatsoever between the number of significant figures of the parameter values in table VII

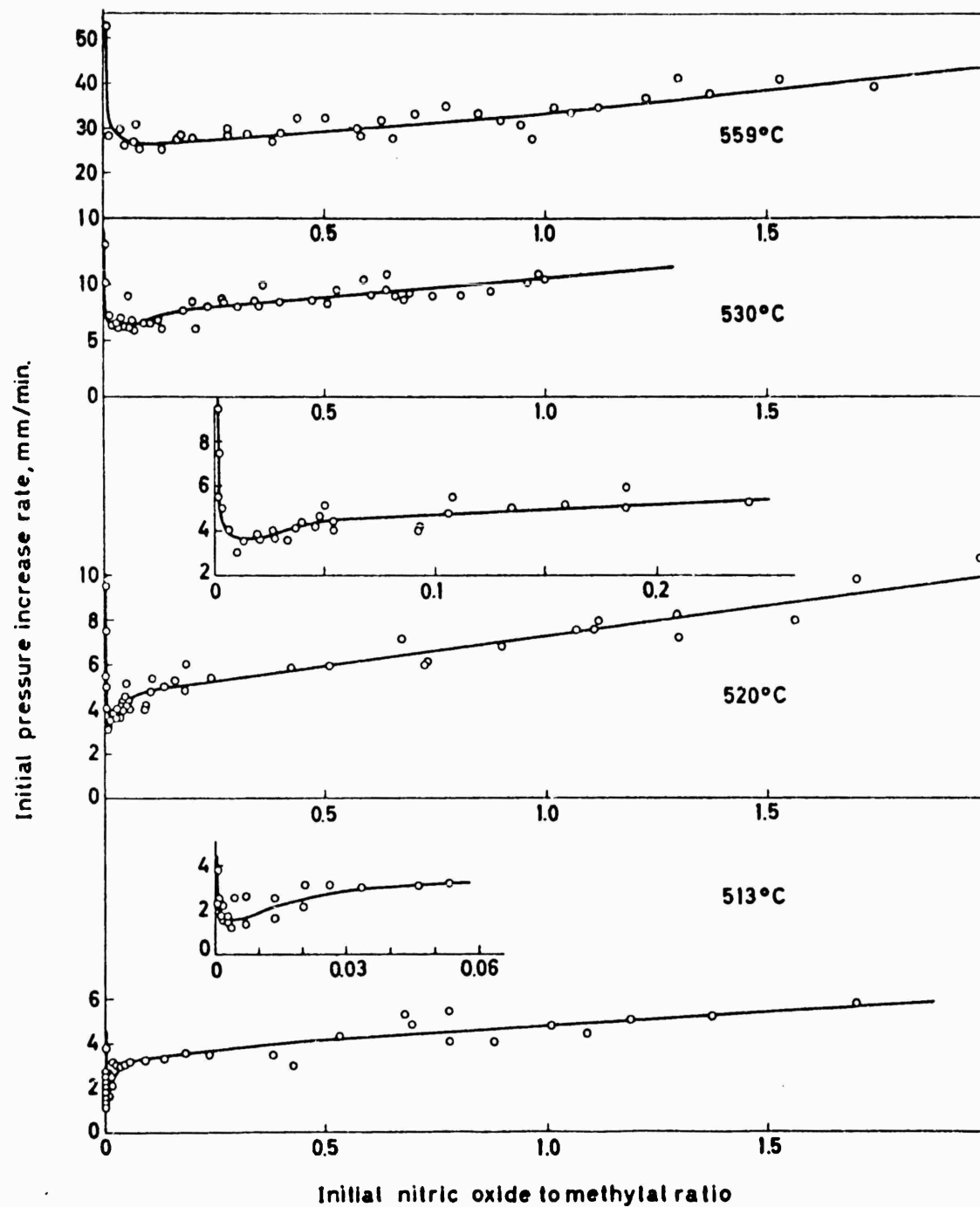


Fig. 24. Experimental points, theoretical curves

and the accuracy of these values as obtained by the trial and error method. The parameters shown in table VII are only the actual values used in the evaluation of the theoretical pressure increase rate-relative amount of nitric oxide curves plotted in fig. 24.

The seven parameters involved in equation [34] may seem too large a number to allow for an accurate determination of their values by the trial and error method. In fact, the error made in the calculation varies largely from one parameter to another and for most of them we can only obtain the order of magnitude.

The order of magnitude of k_{18}/k_5 , a parameter which exerts a considerable influence on the shape of the curve, is well established, the relative error of the values being about 30 %. Moreover the orders of magnitude of the k_{14} and k_6/k_4 parameters, whose influence lies in the fact that their values are critical in determining the slope of the curve for great N/M values, are obtained without any great error.

On the other hand, the values obtained for k_1 are less accurate than

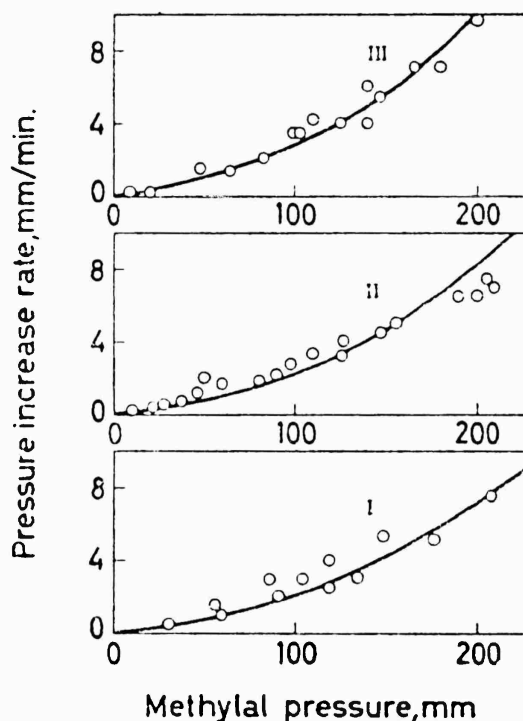


Fig. 25. 520 °C. Experimental points, theoretical curves. Curve I - 1/30; II - 1/10; III - 1/2 nitric oxide to methylal ratio

the preceeding ones. It is only possible to know that k_{15}/k_3 is much greater than k_{18}/k_5 and that it is likely to decrease with increasing temperature. It is even doubtful that the orders of magnitude of k_7/k_8 and $k_{14} k_{17}/k_{16}^2$ are those of the values shown in table VII, owing to the minor importance of these parameters in the adjustment of the curves.

However, the parameters obtained are valuable if considered in their totality because they allow us to obtain a very acceptable adjustment to experimental results for the four temperatures studied. The adjustment has been proved satisfactory both for the low and high values of the nitric oxide to methylal ratios considered, notwithstanding the peculiar shape of the experimental curves.

Equation [34] may be applied to study the variation of $(dp/dt)_0$ for different values of the methylal initial pressure while keeping constant the $(N/M)_0$ ratio. The latter condition would mean that n_A , n_B and n_H were also constant in equation [34].

By making use of the parameters at 520°C in table VII, the theoretical curves for three values of $(N/M)_0 = 1/30, 1/10, 1/2$, have been calculated and plotted in fig. 25. It is worth remarking that the agreement obtained between the theoretical curves and the experimental points is attained by making use of the same parameter values deduced from the experiments made for $M_0 = \text{constant}$ which were plotted in fig. 24.

IV.2.5. The activation energies and the frequency factors of the elementary steps

The seven parameters involved in equation [34] are rate constants or rate constant ratios which allow us to check their values for the four temperatures by means of Arrhenius plots (fig. 26). For comparative and checking purposes the k_6/k_4 , k_7/k_8 and k_1 values at 459°C, deduced from the results obtained for the methylal uninhibited decomposition (5) have also been plotted in the same figure.

The k_1 value at 459°C is only a rough approximation obtained as follows. From equations [5] and [6] in the 2nd Annual Report, the following expression may be obtained:

$$\frac{R}{M} = \frac{k_1 k_8 - k_3 k_{13} H^2}{k_8 k_{11} H}$$

which, together with [32] in the same Report, gives:

$$k_1 > \frac{k_{13}}{k_3 k_8} \left(\frac{V_{II_2}}{2} \right)^2$$

From the data it is not possible to calculate with accuracy the lower limit of k_1 owing to the errors involved in the calculation of $k_{13}/k_3 k_8$, but the order of magnitude of this limit is about 10^{-6} seg^{-1} .

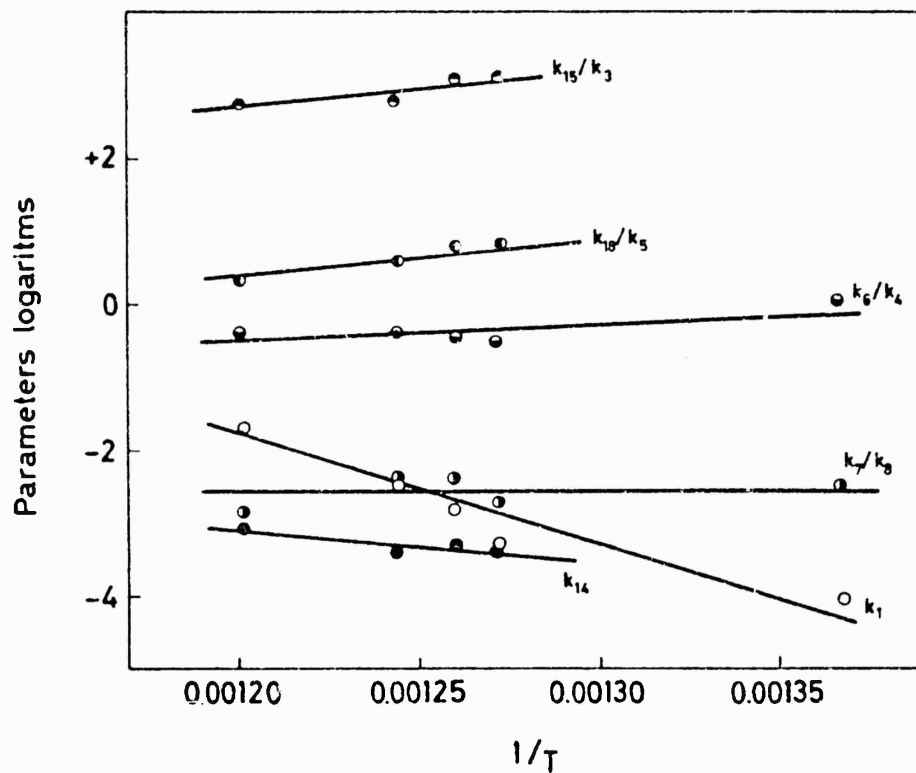


Fig. 26.

From the Arrhenius plots in fig. 26, reasonable values of the corresponding activation energies and frequency factors may be calculated (table VIII).

TABLE VIII

(Activation energies are in Kcal/mol)

E_1	E_{14}	$E_6 - E_4$	$E_7 - E_8$	$E_{18} - E_5$	$E_{15} - E_3$
70	30	-10	0	-18	-20
A_1 (seg^{-1})	A_{14} ($\text{c.c.mol}^{-1} \text{ seg}^{-1}$)	A_6/A_4	A_7/A_8 (c.c.mol^{-1})	A_{18}/A_5	A_{15}/A_3
10^{15}	10^{11}	10^{-3}	1.2×10^5	4×10^{-5}	3×10^{-3}

According to data appearing in the literature (22) (23) (24), $E_{18} \sim 0$, A_{18} being of the order of $10^{10} \text{ c.c. mol}^{-1} \text{ seg}^{-1}$ and taking into account the data obtained by us, a value of $A_5 = 2 \times 10^{14} \text{ c.c. mol}^{-1} \text{ seg}^{-1}$ follows, which is in the range of the more usual values for a bimolecular frequency factor.

IV.2.6. The formation of hydrogen cyanide

From [10 bis] and [21]:

$$\frac{d[\text{HCN}]}{dt} = \frac{k_{20}^2}{4k_{19}} \left[\sqrt{1 + \frac{8k_{18}k_{19}}{k_{20}^2} \frac{N}{k_5M + k_{18}N} \frac{d\text{HCOOCH}_3/dt}}{1} - 1 \right] \quad [35]$$

Quantitative analyses have been made of the hydrogen cyanide and methyl formate formed at 520°C from mixtures of 150 mm initial methylal pressure with variable amounts of initial nitric oxide. Samples have been taken at 8' and 15' reaction time (table IX).

It is unfortunate that the experimental data are not accurate enough to undertake the measurements of the hydrogen cyanide and methyl formate rates and that only the partial pressures of these compounds at some fixed reaction times can be measured. Consequently, the validity of

TABLE IX

520°C. Initial methylal pressure 150 mm
(pressures in mm)

Nitric oxide initial pressure	8 minutes		15 minutes	
	Hydrogen cyanide	Methyl formate	Hydrogen cyanide	Methyl formate
10	0.3	12	-	-
50	0.5	13	1	16
100	0.9	15	1.4	20

equation [35] can not be experimentally checked. However, the above results together with those presented in table VII are not in contradiction

with equation [35] provided the $\frac{k_{20}^2}{k_{10}}$ ratio amounts to only a few mm per minute.

It is worth remarking that the results in table IX justify that the term $2 \frac{d[\text{HCN}]}{dt}$ be neglected in equation [33] as was done before, because

its value amounts only to about 5% of the total $(dp/dt)_0$ value. Moreover, the absolute value of the neglected complete expression $2 \frac{d[\text{HCN}]}{dt} - \frac{d[\text{N}_2\text{O}]}{dt}$

is smaller because the N_2O partial pressures found by analysis are still lower.

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VI. APPENDIX

A. Implications of the results for possible future work

Acetals are important because they can be used to make fuel mixtures and because they increase the octane number of ordinary gasolines. The study of their thermal decomposition was undertaken with the idea that it would be followed by that of their oxidation. There is no doubt that research on these combustion processes would cast a great deal of light on the behaviour of acetals in fuels.

But there is also another interesting possibility for future work that has become increasingly important in the course of the progress of the work already carried out. The points of view of the inhibition of the thermal decomposition of organic compounds seem to justify a revision if the results obtained with the inhibitors used in this research, especially with nitric oxide, are taken into account.

B. Scientific personnel employed during the reporting period

Dr. M. J. Molera, Prof. J. Morcillo, Dr. J. Orza, Mr. L. Arévalo and Mr. E. Gómez-Olea. Also Prof. J. Fernandez-Biarge, a mathematician, has given us much help in the theoretical part of this research.

C. Manhours expended on the contract

Dr. M. J. Molera, one year work, at 90 hours per month

Prof. J. Morcillo, one year work, at 45 hours per month

Dr. J. Orza, one year work, at 180 hours per month

Mr. L. Arévalo, eight months work, at 180 hours per month

Mr. E. Gómez-Olea, four months work, at 180 hours per month.

From the above relation, and taking into account vacations and official holidays, we arrive at an estimated number of about 5500 manhours.

D. Materials expended in carrying out the contract

About \$ 150 in chemicals and other expendable supplies.

E. Apparatus

No important property has been acquired during the reporting period at direct contract expense.